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Towards High Performance p-Type Transparent Conducting Oxides

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Towards High Performance p-type Transparent Conducting Oxides

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ABSTRACT

P-type transparent conductive oxides would have potential applications in photovoltaics, transparent electronics and organic opto-electronics. In this paper we present results on the synthesis of Cu_2SrO_2, a p-type transparent conducting oxide, by a chemical solution route as well as the conventional pulse laser deposition (PLD) method. For Cu_2SrO_2 by the chemical solution route, samples were made by spraying deposition on quartz substrates using an aqueous solution of Copper formate and Strontium acetate. Phase pure materials were obtained by an optimum two stage annealing sequence. This initial work led to the development of good quality homogeneous films by a related sol-gel approach. We have also used pulsed laser depostion (PLD) to deposit Cu_2SrO_2 and $CuInO_2$ thin films on quartz substrates. We have obtained improved conductivities in the $CuInO_2$ thin films over previously published work. We present details on the nature of the relationship of process parameters to the opto-electronic properties of the films.

1. INTRODUCTION

Although n-type TCO's such as ZnO, SnO_2 and ITO are key components in a variety of technologies, p-type TCO's are an emerging area with little work previous to four years ago. However, realization of good TCO could significantly impact a new generation of transparent electrical contacts for p-type semiconductors and organic optoelectronic materials and in conjunction with n-type TCOs could lead to a next generation of transparent electronics.

Work by the groups of Kawazoe and Hosono over the last few years have led to the description of a number of p-type TCOs [1-4] based on the Cu_2O structure. Many of these results originally done by PLD have been difficult to reproduce but were potentially enabling to the applications above. Cu_2SrO_2 was deposited [3] under working oxygen pressure of 5.25 x 10^{-3} mTorr and 300 $^{\circ}$C . $CuInO_2$ was deposited [4] under working oxygen pressure of 7.5 mTorr and 450 °C . Conductivity of the $CuInO_2$ film [4] was reported as 2.8x 10^{-3} S/cm.

In this paper we discuss our work to improve upon the earlier work in Japan by PLD for Cu_2SrO_2 and $CuInO_2$ thin films and to expand our approach for the first time to atmospheric process methods for deposition of Cu_2SrO_2.

2. Solution Deposition of Cu_2SrO_2

To accomplish this we utilized the extensive work on the Cu-Sr phase diagram that came primarily out of work on the HTS materials. Thus there has been considerable interest in phase relations for Cu-Sr-O and related systems [5-9] since 90's. The phase diagram (Fig. 1) drawn according to Suzuki et. al.[8] for Cu:Sr ratio 2:1, shows that it is possible to get Cu_2SrO_2 phase from CuO and SrO within an accessible range of temperature and pressure. That phase diagram served as the starting point of our project. Our first aim was to develop an optimum annealing protocol that would produce phase pure materials. Copper formate ($Cu(CH_3COO)_2$) and Strontium acetate ($Sr(CH_3COO)_2$) were chosen as starting precursors. Stoichiometric amounts of Copper formate and Strontium acetate were prepared as separate aqueous solutions and mixed just before application (otherwise copper acetate precipitated) and were sprayed on quartz substrates at ~250 °C. These samples were essentially powders that weakly adhered to the glass. Thickness of the films were measured by stylus profile meter (Dektak^3), crystalline phases were identified by X-Ray diffraction (Cu Kα, XGEN-4000, SCINTAG INC., USA). Films of various thicknesses were prepared and characterized as T1(36μ)>T2(13μ) >T3(4.5μ) >T4(3.7μ). Samples were annealed at 775 °C, for 3 and 1/2 hours at 1.0 x 10^{-2} mTorr oxygen pressure. Fig.2 shows the XRD patterns of the samples along with the lines from the standard PDF files .

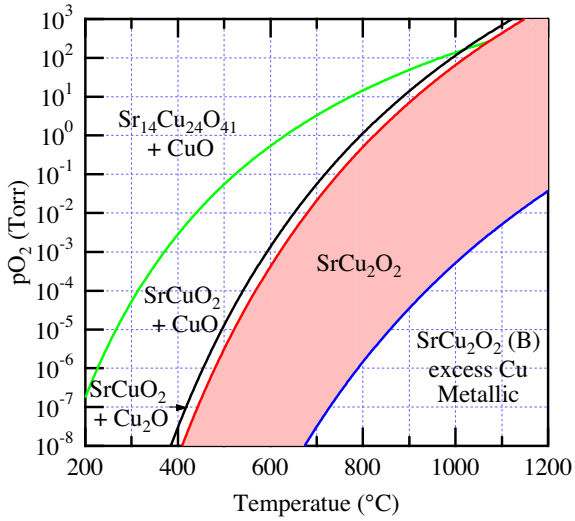

Figure 1. Sr-Cu-O Phase diagram for Cu:Sr=2:1

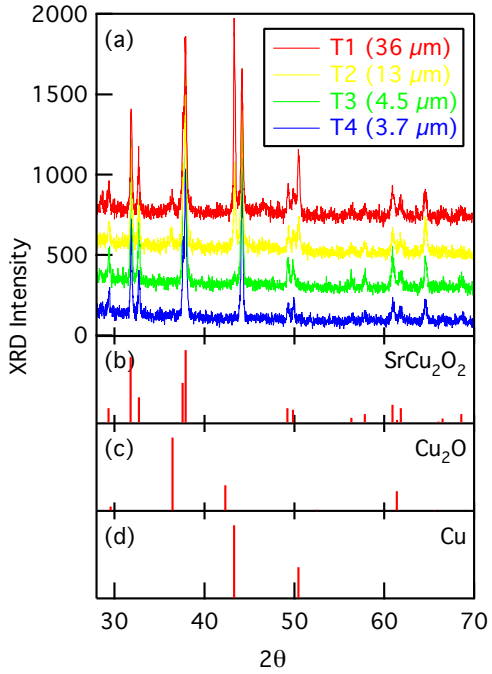

Figure 2. Variation of phase content with increasing of thickness for sprayed Cu_2SrO_2 samples.

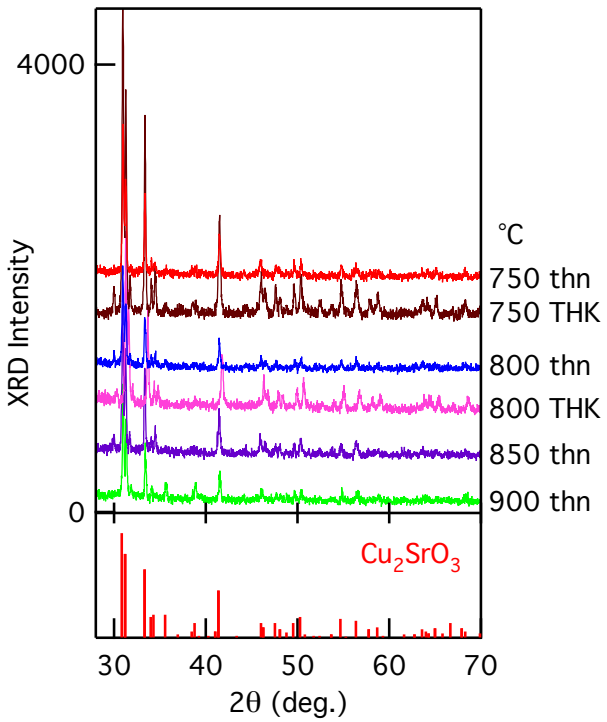

Figure 4. XRD Diagrams of air annealed Cu_2SrO_2 spray samples

As the thickness of the films increases, the amount of second phase (Cu and /or Cu_2O) increases. For the samples of thickness 4.5 μ (T3) and 3.7 μ (T4) amount of Cu and Cu_2O are negligible, but for the thicker samples (T2 and T1), amount of second phases becomes significant.

TGA analysis of (Fig. 3) Cu-formate, Sr-Acetate and mixture of Cu-formate and Sr-Acetate was performed from room temperature to 1000°C. The results show that for Cu-formate initial loss of water and organics occurs around 100 °C and 250 °C respectively. For Sr-acetate water loss occurs around 200^{0}C, decomposition of organics is not until 400^{0}C, and decomposition of $Sr(CO_3)_2$ occurs around 900 ^{0}C. While for the mixture of the two precursors, water loss is the same, the main reaction occurs around 750^{0}C. Above 750 °C, only Cu_2SrO_3 phase exists which had been confirmed by X-Ray diffraction.

Figure 4 shows the X-Ray diffraction data for the samples sprayed on quartz substrates at 250^0 C and annealed at different temperature for 30 minutes in air to remove the organic component and minimize carbon impurities. Up to

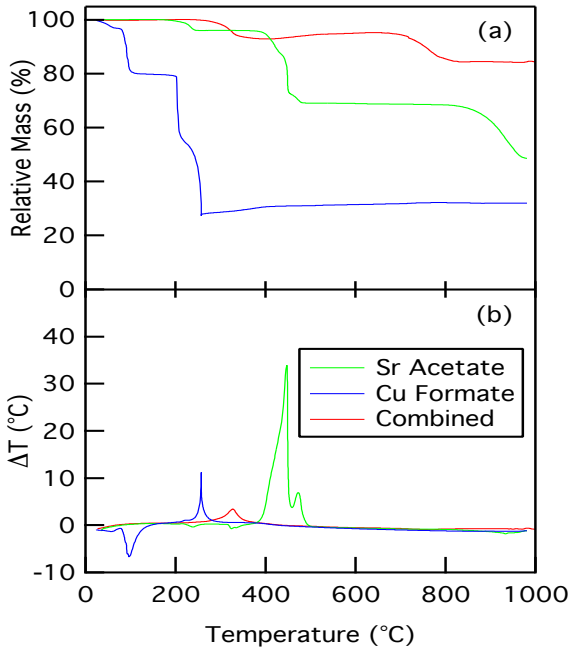

Figure 3. (a) DTA and (b) TGA curves for Cu, Sr and mixed precursors

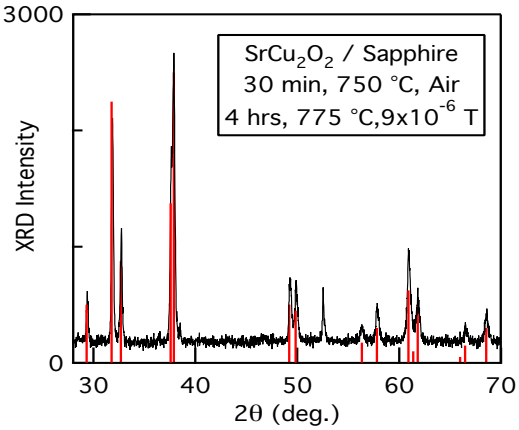

Figure 5. XRD Diagram for Cu_2SrO_2 sample after final PLD annealing along with PDF standard lines

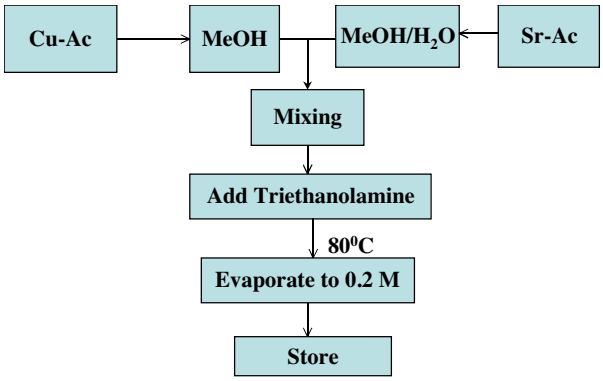

Figure 6. Flow chart diagram for preparing precursor sol for Cu_2SrO_2 sol

900^0C the product was always Cu_2SrO_3 regardless of the thickness of the samples. But for quartz substrate, there were significant problems with film adherence. These might be the result of a difference in thermal expansion coefficient of quartz substrate and Cu_2SrO_3 phase.

Subsequent samples were grown on sapphire (1102) substrates. Samples were sprayed from aqueous solution with the same precursors. Films were preannealed at ~ 750 °C for 30 mins in air and then finally annealed at 775^0C , for 4 hrs in our PLD system (better atmospheric control) under working oxygen pressure 9 x 10^{-3} mTorr. Thickness of the films was around 40 μ. Figure 5 shows the XRD of the sample after final annealing and the standard PDF data for the Cu_2SrO_2 phase indicating phase pure material.

The next step was to transition the process for making phase pure materials to that for smooth adhering films. To accomplish this we are investigating the application of sol-gel processing of the same kind of precursors. Figure 6 shows a flow-chart for preparing the sol for Cu_2SrO_2 thin films. Stored precursor sol (as in Fig. 6) was diluted by isopropyl alcohol and spin coated on MgO(100) substrates for 20 sec, at 3000rpm . After coating,

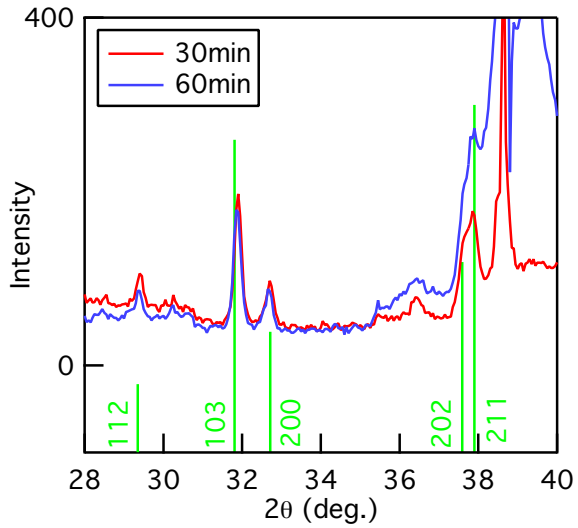

Figure 7. XRD patterns of spin coated Cu_2SrO_2 films along with standard PDF lines

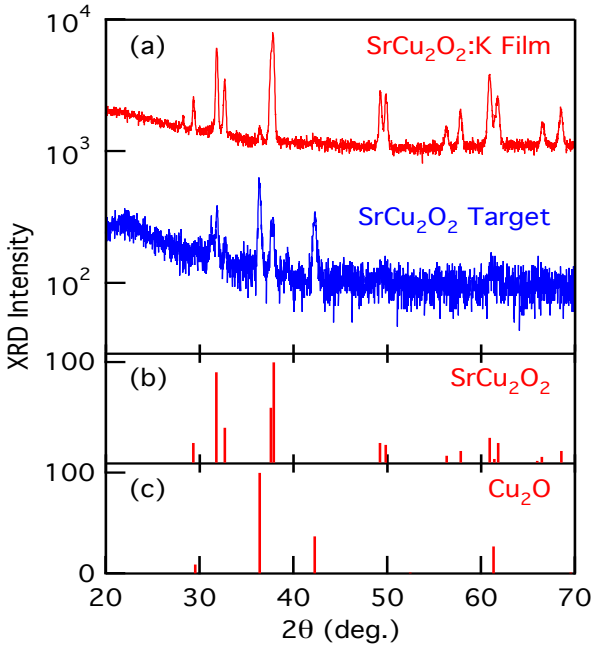

Figure 8. XRD patterns of PLD target and film of Cu_2SrO_2 along with standard PDF lines

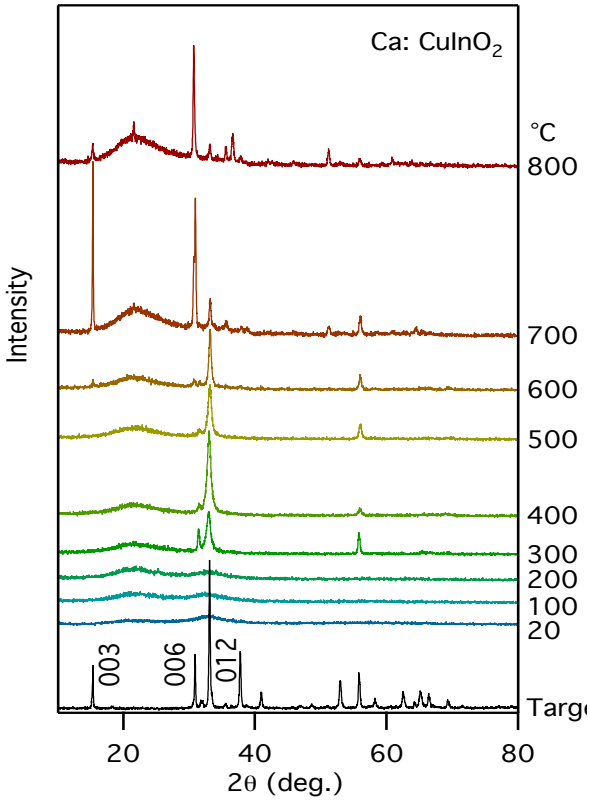

Figure 9. XRD patters of $CuInO_2$ target and films deposited at different temperatures

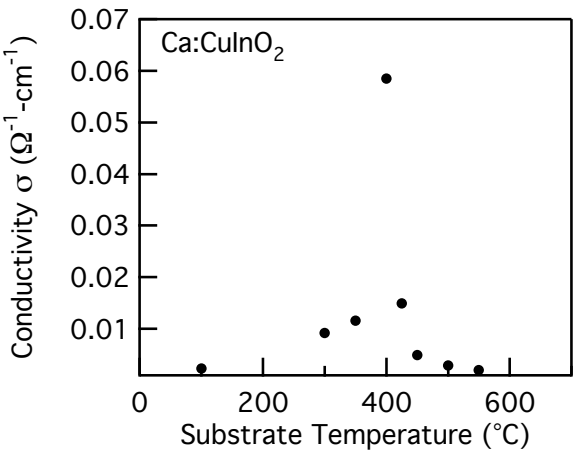

Figure 10. Dependence of electrical conductivity of $CuInO_2$ films on deposition temperature

the resultant film was annealed at 200^0C temperature for 2 min and then pyrolysed at 500 °C for 2 minutes. The spin coating and pyrolysis cycle was repeated 8-10 times. After all deposition cycles the film was annealed at 750^0C for 30 min in air and then, finally annealed at 775^0C under 2.7 x 10^{-3} mTorr oxygen. These films showed significantly enhanced smoothness and adherence over those from the spray pyrolysis approach. Fig. 7 Shows the XRD patterns of the sol-gel films as a function of processing time. FTIR reflection spectra measured up to 10μm showed no indication of the plasma edge consistent with the essentially undoped nature of the films.

3 PLD results:

A 1-inch diameter Cu_2SrO_2 target was cold pressed from a ball milled stoichiometric mixture of Cu_2O and SrO powder. The green target was sintered at 800^0C temperature in an Ar atmosphere for 10 hrs. This sintered mass was reground in a ball mill and resintered twice. A 1.6% K-doped Cu_2SrO_2 target was made in the same way. Films were deposited using KrF (248nm) laser on fused quartz substrates under working oxygen pressure of 70 mTorr and at 650^0C. Deposited films were annealed at 775^0 C for 6 hrs under oxygen pressure of 1.6 x 10^{-3} mTorr.

Figure 8 shows the XRD patterns of the annealed K-doped Cu_2SrO_2 film and undoped Cu_2SrO_2 target Where the target is phase pure Cu_2SrO_2, the resultant film is a mixture of Cu_2SrO_2 and Cu_2O, corresponding to the narrow band next to the Cu_2SrO_2 phase in Fig. 1. It was difficult to obtain phase pure materials by this approach.

A 5% Ca-doped $CuInO_2$ target was prepared by cation exchange method by the Hosono group a TIT. Detail of the target preparation procedure has been discussed in somewhere else[4]. $CuInO_2$ films were deposited using KrF (248nm) laser on fused quartz substrates under working oxygen pressure of 7.5 mTorr at different temperatures. Thickness of the films was measured by stylus profile meter (Dektak[3]), Crystalline phases were identified by X-Ray diffraction (Cu Kα, XGEN-4000, SCINTAG INC., USA), and conductivity was measured by four-probe method.

Figure 9 shows the XRD patterns of the films deposited in the temperature range 25 °C to 800 °C . Films deposited at lower temperatures appear to be amorphous. For films deposited in the range of temperature from 300 °C to 600 °C all of the resultant XRD peaks could be identified as arising from $CuInO_2$ delafossite[10]. For the films deposited at temperatures above 600^0C , XRD indicates that the film is a mixture of $CuInO_2$ and In_2O_3. This result is consistent with previous work of Yanagi et. al. [4].

Figure 10 shows the dependence of the electrical conductivity of $CuInO_2$ films upon the deposition temperature. With increasing deposition temperature, conductivity increases and reaches a value of 5.8 x 10^{-2} S/cm for the film deposited at 400^0C temperature which is significantly better than previously published results.

4. Summary

We have demonstrated the ability to make phase pure p-type TCOs by a variety of methods. We have demonstrated for the first time the sol-gel synthesis of a p-type TCO. Improved electrical properties have been obtained for PLD deposited films. Future work will focus on the doping and low temperature processing of these materials.

REFERENCES

[1] H. Kawazoe, M. Yasukawa, H. Hyodo, M. Kurita, H. Yanagi, and H. Hosono, *Nature* , **389**, p 939 (1997)

[2] H. Yanagi, H. Kawazoe, A. Kudo, M. Yasukawa, and H. Hosono, *J. Electroceram*., **4**, p 427 (2000)

[3] A. Kudo, H. Yanagi, H. Hosono, H. Kawazoe, *Appl. Phys. Lett*. **73.,** p 220 (1998).

[4] H. Yanagi, T. Hase, S. Ibuki, K. Ueda, and H. Hosono, *Appl. Phys. Lett.,* **78** [11], p 1583 (2001).

[5] R.S. Roth, C.J. Rawn, J.J. Ritter, and B.P. Burton, *JACS*, **72** [8], P 1545 (1989)

[6] C.B. Alcock and B. Li, *JACS*, **73**[5], P1176 (1990).

[7] N.M. Hwang, R.S. Roth, and C.J. Rawn, *JACS,* **73**[8], P2531 (1990).

[8] R.O. Suzuki, P. Bohac, and L.J. Gauckler, *JACS,* **75** [10], P 2833 (1992).

[9] K.T. Jacob and T. Mathews, *JACS*, **75**[12], P 3225 (1992).

[10] M. Shimode, M. Sasaki, and K. Mukaida, *J. Solid state Chem*., **151**, p 16 (2000).

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P-type transparent conductive oxides would have potential applications in photovoltaics, transparent electronics and organic opto-electronics. In this paper we present results on the synthesis of Cu2SrO2, a p-type transparent conducting oxide, by a chemical solution route as well as the conventional pulse laser deposition (PLD) method. For Cu2SrO2 by the chemical solution route, samples were made by spraying deposition on quartz substrates using an aqueous solution of Copper formate and Strontium acetate. Phase pure materials were obtained by an optimum two stage annealing sequence. This initial work led to the development of good quality homogeneous films by a related sol-gel approach. We have also used pulsed laser depostion (PLD) to deposit Cu2SrO2 and CuInO2 thin films on quartz substrates. We have obtained improved conductivities in the CuInO2 thin films over previously published work. We present details on the nature of the relationship of process parameters to the opto-electronic properties of the films.

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